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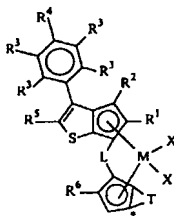
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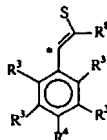
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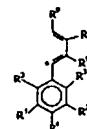
(54) Title: PROCESS FOR THE COPOLYMERIZATION OF ETHYLENE



(I)



(II)



(III)

(57) Abstract: A process for producing a polymer of ethylene containing from 0.1 to 99 % by mol of one or more derived units of alpha-olefins and optionally from 0 to 5% by mol polyene, comprising contacting, under polymerization conditions, ethylene, one or more alphaolefins and optionally said polyene, in the presence of a catalyst system obtainable by contacting: a) a metallocene compound of formula (I): wherein M is zirconium, hafnium or titanium; X, is a hydrogen atom, a halogen atom, or a hydrocarbon group; R<sup>1</sup> is a hydrocarbon group; R<sup>2</sup>, R<sup>3</sup>, R<sup>4</sup> and R<sup>5</sup>, equal to or different from each other, are hydrogen atoms, or hydrocarbon groups; R<sup>6</sup> is a hydrocarbon group; L is a divalent bridging group, and T is a divalent radical of formula (II) or (III): wherein R<sup>8</sup> and R<sup>9</sup> are hydrogen or hydrocarbon groups; and b) an alumoxane or a compound capable of forming an alkyl metallocene cation.

## PROCESS FOR THE COPOLYMERIZATION OF ETHYLENE

The present invention relates to a process for the polymerization of ethylene and one or more alpha-olefins of formula  $\text{CH}_2=\text{CHZ}$ , wherein Z is a  $\text{C}_2\text{-C}_{20}$  alkyl radical, in the presence of a metallocene catalyst.

It is known that polyethylene can be modified by the addition, during the polymerization reaction, of small quantities of alpha-olefins, generally 1-butene, 1-hexene or 1-octene. This gives LLDPE (linear low density polyethylene) copolymers which have short branches along the main chain due to the units derived from the alpha-olefin comonomers. These branches have the effect that the degree of crystallinity and hence the density of copolymer turn out to be lower than in polyethylene homopolymer. Typically, the LLDPE copolymers have densities of the order of  $0.915\text{-}0.940\text{ g/cm}^3$ . Consequently, the LLDPE copolymers have advantageous mechanical properties, in particular for the production of films.

The lowering of the degree of crystallinity and of the density of the copolymers depends on the type and quantity of the incorporated alpha-olefin. In particular, the greater the quantity of incorporated alpha-olefin, the lower are the resulting degrees of crystallinity and density. Besides the type and quantity of the incorporated alpha-olefin comonomer, the properties of the copolymer depend on the distribution of the branches along the polymer chain. In particular, a uniform distribution of the branches has relevant effects on the properties of the copolymers. In fact, with the same type and quantity of incorporated alpha-olefin, a higher uniformity of distribution allows lower degrees of crystallinity and density to be obtained.

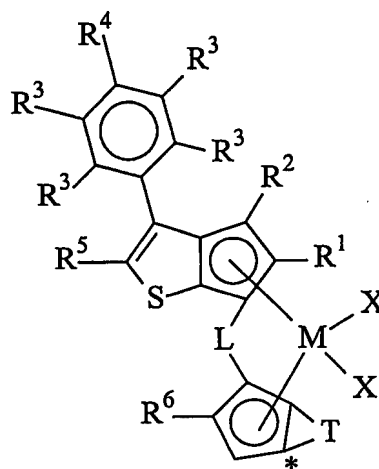
Metallocene compounds having two bridged cyclopentadienyl groups are known as catalyst components for the homo- and copolymerization reaction of ethylene. A drawback of the use of metallocene catalysts is that the comonomer incorporation ability is quite low, and therefore it is necessary to use a large excess of comonomer in order to achieve copolymers having the desired comonomer content. Moreover, it is desirable to have a metallocene compound having a high activity in terms of obtained polymer, and a good comonomer incorporation ability so that it is sufficient to use a small excess of comonomer in the reactor; it is also desirable to find a metallocene catalyst able to give copolymers having a high molecular weight.

In WO 01/44318 it is described a new class of metallocene compounds in which the  $\pi$  ligands are substituted thiopentalenes; in this document there are no examples relating to LLDPE polymers.

The applicant has now found a class of metallocene compounds having a good balance of the above-mentioned technical effects and in a special way having a high activity.

According to a first aspect of the present invention, it is provided a process for producing a polymer of ethylene containing from 0.1 to 99 % by mol of one or more derived units of alpha-olefins of formula  $\text{CH}_2=\text{CHZ}$ , wherein Z is a  $\text{C}_2\text{-C}_{20}$  alkyl radical, and optionally from 0% to 5% by mol polyene, comprising contacting, under polymerization conditions, ethylene, one or more alpha-olefins and optionally said polyene, in the presence of a catalyst system obtainable by contacting:

a) a metallocene compound of formula (I):



(I)

wherein

M is zirconium, hafnium or titanium;

X, equal to or different from each other, is a hydrogen atom, a halogen atom, a R, OR, OR'O, OSO<sub>2</sub>CF<sub>3</sub>, OCOR, SR, NR<sub>2</sub> or PR<sub>2</sub> group, wherein R is a linear or branched, saturated or unsaturated C<sub>1</sub>-C<sub>20</sub>-alkyl, C<sub>3</sub>-C<sub>20</sub>-cycloalkyl, C<sub>6</sub>-C<sub>20</sub>-aryl, C<sub>7</sub>-C<sub>20</sub>-alkylaryl, or C<sub>7</sub>-C<sub>20</sub>-arylalkyl radical, optionally containing one or more heteroatoms belonging to groups 13-17 of the Periodic Table of the Elements; and the R' substituent is a divalent group selected from C<sub>1</sub>-C<sub>40</sub>-alkylidene, C<sub>6</sub>-C<sub>40</sub>-arylidene, C<sub>7</sub>-C<sub>40</sub>-alkylarylidene or C<sub>7</sub>-C<sub>40</sub>-arylalkylidene radicals; two X can also join to form a C<sub>4</sub>-C<sub>40</sub> dienyl ligand, preferably a 1-3 dienyl ligand; examples of C<sub>1</sub>-C<sub>20</sub> alkyl radicals are methyl, ethyl, n-propyl, isopropyl, n-butyl, i-butyl, s-

butyl, t-butyl, n-pentyl, n-hexyl, n-heptyl and n-octyl radicals; examples of C<sub>3</sub>-C<sub>20</sub>-cycloalkyl radicals are cyclopentyl and cyclohexyl;

preferably X is a halogen atom, a R, OR'O or OR group; more preferably X is chlorine or methyl;

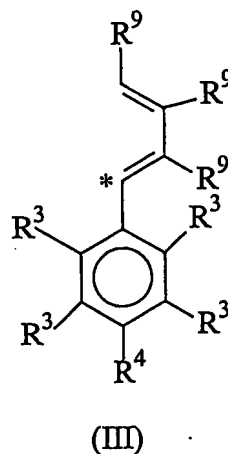
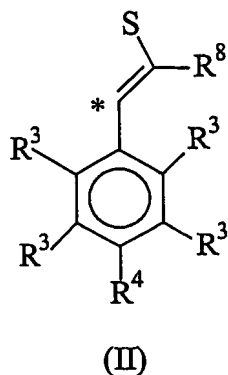
R<sup>1</sup> is a linear or branched, saturated or unsaturated C<sub>1</sub>-C<sub>20</sub>-alkyl, C<sub>3</sub>-C<sub>20</sub>-cycloalkyl, C<sub>6</sub>-C<sub>20</sub>-aryl, C<sub>7</sub>-C<sub>20</sub>-alkylaryl, or C<sub>7</sub>-C<sub>20</sub>-arylalkyl radical, optionally containing one or more heteroatoms belonging to groups 13-17 of the Periodic Table of the Elements; preferably R<sup>1</sup> is a linear or branched, saturated or unsaturated C<sub>1</sub>-C<sub>20</sub>-alkyl radical;

R<sup>2</sup>, R<sup>3</sup>, R<sup>4</sup> and R<sup>5</sup>, equal to or different from each other, are hydrogen atoms, halogen atoms or linear or branched, saturated or unsaturated C<sub>1</sub>-C<sub>20</sub>-alkyl, C<sub>3</sub>-C<sub>20</sub>-cycloalkyl, C<sub>6</sub>-C<sub>20</sub>-aryl, C<sub>7</sub>-C<sub>20</sub>-alkylaryl, or C<sub>7</sub>-C<sub>20</sub>-arylalkyl radicals, optionally containing one or more heteroatoms belonging to groups 13-17 of the Periodic Table of the Elements; preferably R<sup>2</sup> is a hydrogen atom; preferably R<sup>3</sup> is a hydrogen atom or a linear or branched, saturated or unsaturated C<sub>1</sub>-C<sub>20</sub>-alkyl radical optionally containing one or more halogen atom; preferably R<sup>4</sup> is a hydrogen atom or a linear or branched, saturated or unsaturated C<sub>1</sub>-C<sub>20</sub>-alkyl radical, more preferably R<sup>4</sup> is hydrogen or a group -C(R<sup>7</sup>)<sub>3</sub>, wherein R<sup>7</sup>, equal to or different from each other, is a linear or branched, saturated or unsaturated C<sub>1</sub>-C<sub>8</sub>-alkyl radical; and preferably R<sup>5</sup> is a linear or branched, saturated or unsaturated C<sub>1</sub>-C<sub>10</sub>-alkyl radical;

R<sup>6</sup> is a linear or branched, saturated or unsaturated C<sub>1</sub>-C<sub>20</sub>-alkyl, C<sub>3</sub>-C<sub>20</sub>-cycloalkyl, C<sub>6</sub>-C<sub>20</sub>-aryl, C<sub>7</sub>-C<sub>20</sub>-alkylaryl, or C<sub>7</sub>-C<sub>20</sub>-arylalkyl radical, optionally containing one or more heteroatoms belonging to groups 13-17 of the Periodic Table of the Elements; preferably R<sup>6</sup> is a linear or branched, saturated or unsaturated C<sub>1</sub>-C<sub>20</sub>-alkyl radical;

L is a divalent bridging group selected from C<sub>1</sub>-C<sub>20</sub> alkylidene, C<sub>3</sub>-C<sub>20</sub> cycloalkylidene, C<sub>6</sub>-C<sub>20</sub> arylidene, C<sub>7</sub>-C<sub>20</sub> alkylarylidene, or C<sub>7</sub>-C<sub>20</sub> arylalkylidene radicals, optionally containing heteroatoms belonging to groups 13-17 of the Periodic Table of the Elements, or it is a silylidene radical containing up to 5 silicon atoms, such as SiMe<sub>2</sub> and SiPh<sub>2</sub>; preferably L is Si(CH<sub>3</sub>)<sub>2</sub>, SiPh<sub>2</sub>, SiPhMe, SiMe(SiMe<sub>3</sub>), CH<sub>2</sub>, (CH<sub>2</sub>)<sub>2</sub>, (CH<sub>2</sub>)<sub>3</sub>, C(CH<sub>3</sub>)<sub>2</sub>, C(Ph)<sub>2</sub> or C(CH<sub>3</sub>)(Ph);

T is a divalent radical of formula (II) or (III):



wherein

the atom marked with the symbol \* is linked to the atom marked with the same symbol in the compound of formula (I);

$R^3$  and  $R^4$  have the meaning previously described;

$R^8$  is a hydrogen atom or a linear or branched, saturated or unsaturated  $C_1$ - $C_{20}$ -alkyl,  $C_3$ - $C_{20}$ -cycloalkyl,  $C_6$ - $C_{20}$ -aryl,  $C_7$ - $C_{20}$ -alkylaryl, or  $C_7$ - $C_{20}$ -arylalkyl radical, optionally containing one or more heteroatoms belonging to groups 13-17 of the Periodic Table of the Elements; preferably  $R^8$  is hydrogen or a linear or branched, saturated or unsaturated  $C_1$ - $C_{20}$ -alkyl;

$R^9$ , equal to or different from each other, is a hydrogen atom or a linear or branched, saturated or unsaturated  $C_1$ - $C_{20}$ -alkyl,  $C_3$ - $C_{20}$ -cycloalkyl,  $C_6$ - $C_{20}$ -aryl,  $C_7$ - $C_{20}$ -alkylaryl, or  $C_7$ - $C_{20}$ -arylalkyl radical, optionally containing one or more heteroatoms belonging to groups 13-17 of the Periodic Table of the Elements; preferably  $R^9$  is hydrogen or a linear or branched, saturated or unsaturated  $C_1$ - $C_{20}$ -alkyl radical;

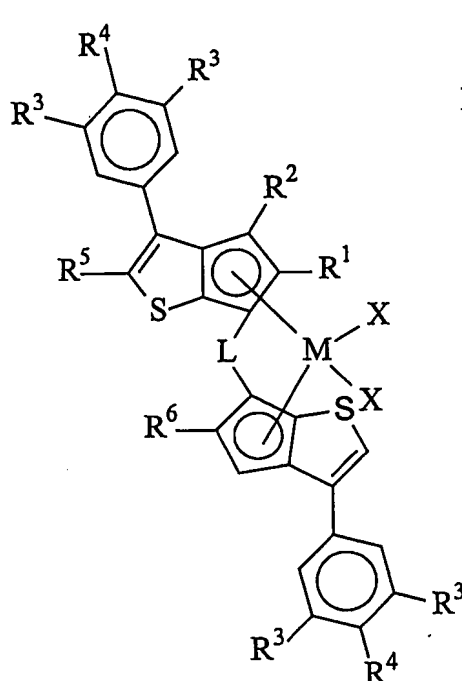
b) an alumoxane or a compound capable of forming an alkyl metallocene cation; and optionally

c) an organo aluminum compound.

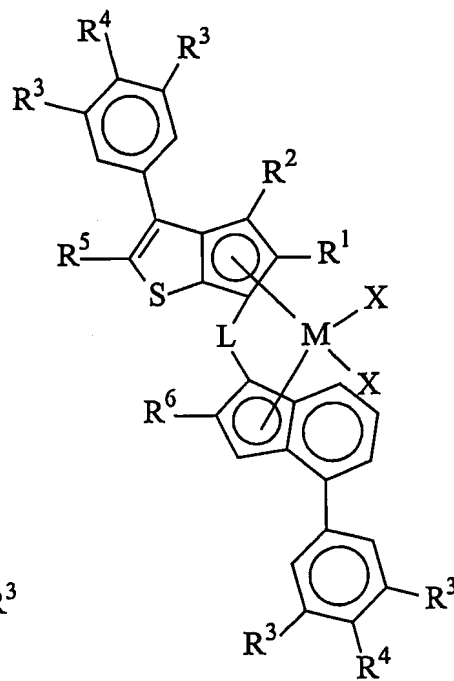
Preferably the metallocene compound of formula (I) is in the racemic form.

Preferred radicals of group T are those of formula (II).

In a particular embodiment, the compound of formula (I) has formulas (IV) or (V):



(IV)



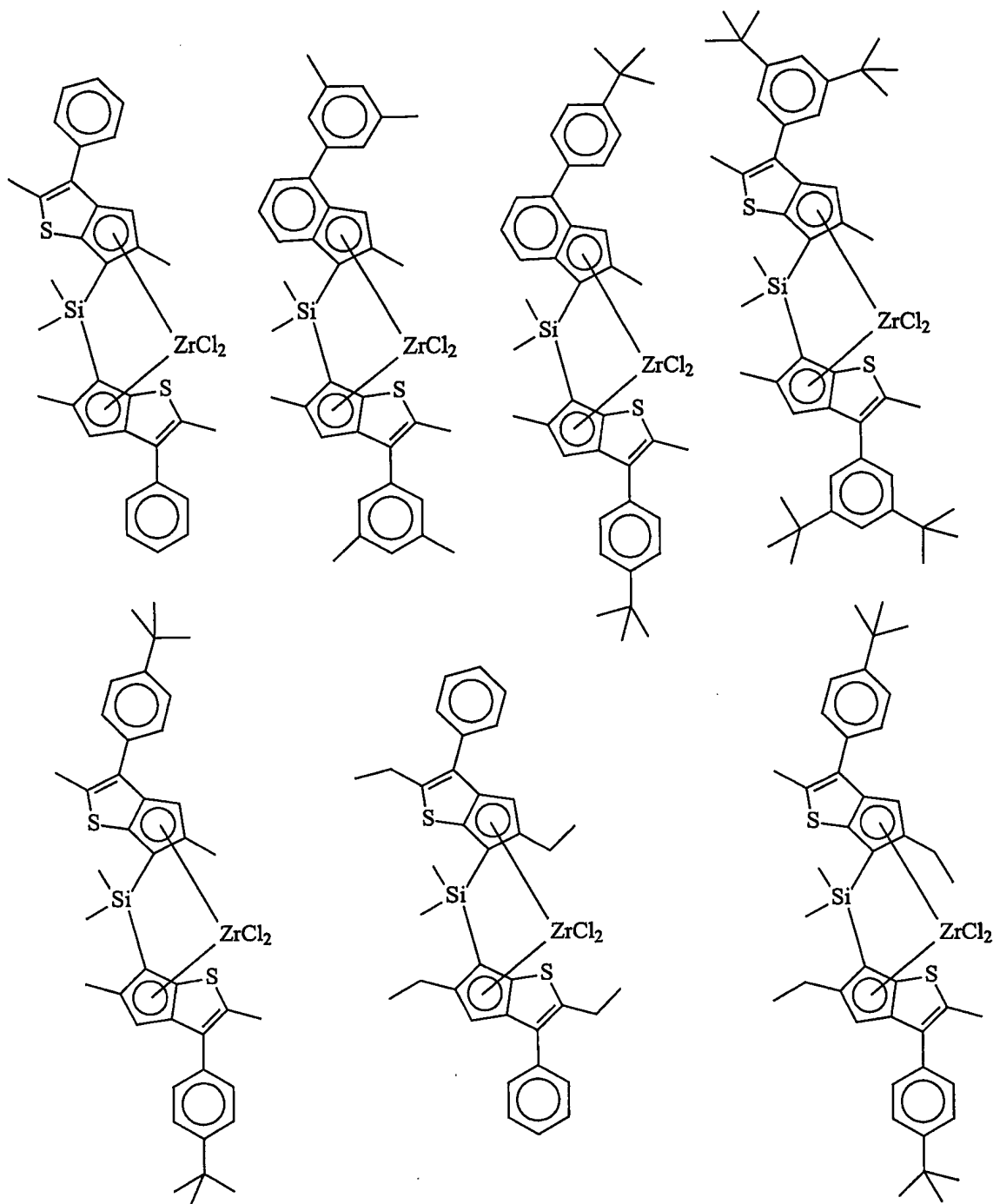
(V)

wherein  $R^1$ ,  $R^2$ ,  $R^5$ ,  $R^6$ ,  $L$ ,  $M$  and  $X$  have been described above;

$R^3$  is a hydrogen atom or a linear or branched, saturated or unsaturated  $C_1$ - $C_{10}$ -alkyl radical, optionally containing one or more halogen atom; more preferably  $R^3$  is a hydrogen atom or a group  $-C(R^7)_3$ , wherein  $R^7$ , equal to or different from each other, is a linear or branched, saturated or unsaturated  $C_1$ - $C_8$ -alkyl radical;  $R^4$  is a hydrogen atom or a linear or branched, saturated or unsaturated  $C_1$ - $C_{10}$ -alkyl radical, more preferably  $R^4$  is hydrogen or a group  $-C(R^7)_3$ , wherein  $R^7$ , equal to or different from each other, is a linear or branched, saturated or unsaturated  $C_1$ - $C_8$ -alkyl radical;

In a further embodiment of the compounds of formulas (IV) and (V),  $R^3$  and  $R^4$  are hydrogen atoms. In another embodiment of the compounds of formulas (I), (IV) and (V), when  $R^3$  is an hydrogen atom,  $R^4$  is a linear or branched, saturated or unsaturated  $C_1$ - $C_{10}$ -alkyl radical optionally containing one or more halogen atom; or when  $R^3$  is a linear or branched, saturated or unsaturated  $C_1$ - $C_{10}$ -alkyl radical, optionally containing one or more halogen atom,  $R^4$  is an hydrogen atom.

Non limiting examples of compounds of formula (I) are:



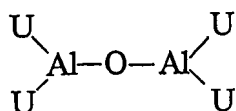
Compounds of formula (I) can be prepared as described in WO 01/44318, EP 02075757.1, EP01204624.9 and EP01202930.2.

Alumoxanes used as component b) can be obtained by reacting water with an organo-aluminium compound of formula  $H_jAlU_{3-j}$  or  $H_jAl_2U_{6-j}$ , where the U substituents, same or different, are hydrogen atoms, halogen atoms,  $C_1$ - $C_{20}$ -alkyl,  $C_3$ - $C_{20}$ -cycloalkyl,  $C_6$ - $C_{20}$ -aryl,  $C_7$ - $C_{20}$ -alkylaryl or  $C_7$ - $C_{20}$ -arylalkyl radicals, optionally containing silicon or germanium atoms, with the proviso that at least one U is different from halogen, and j ranges from 0 to 1, being

also a non-integer number. In this reaction the molar ratio of Al/water is preferably comprised between 1:1 and 100:1.

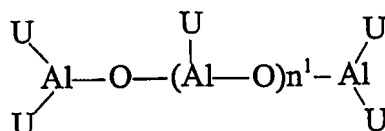
The molar ratio between aluminium and the metal of the metallocene generally is comprised between about 10:1 and about 30,000:1, preferably between about 100:1 and about 5,000:1.

The alumoxanes used in the catalyst according to the invention are considered to be linear, branched or cyclic compounds containing at least one group of the type:

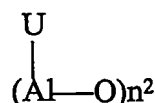


wherein the substituents U, same or different, are described above.

In particular, alumoxanes of the formula:



can be used in the case of linear compounds, wherein  $n^1$  is 0 or an integer of from 1 to 40 and the substituents U are defined as above, or alumoxanes of the formula:



can be used in the case of cyclic compounds, wherein  $n^2$  is an integer from 2 to 40 and the U substituents are defined as above.

Examples of alumoxanes suitable for use according to the present invention are methylalumoxane (MAO), tetra-(isobutyl)alumoxane (TIBAO), tetra-(2,4,4-trimethylpentyl)alumoxane (TIOAO), tetra-(2,3-dimethylbutyl)alumoxane (TDMBAO) and tetra-(2,3,3-trimethylbutyl)alumoxane (TTMBAO).

Particularly interesting cocatalysts are those described in WO 99/21899 and in WO01/21674 in which the alkyl and aryl groups have specific branched patterns.

Non-limiting examples of aluminium compounds according to WO 99/21899 and WO01/21674 are:

tris(2,3,3-trimethyl-butyl)aluminium, tris(2,3-dimethyl-hexyl)aluminium, tris(2,3-dimethyl-butyl)aluminium, tris(2,3-dimethyl-pentyl)aluminium, tris(2,3-dimethyl-heptyl)aluminium, tris(2-methyl-3-ethyl-pentyl)aluminium, tris(2-methyl-3-ethyl-hexyl)aluminium, tris(2-methyl-3-ethyl-heptyl)aluminium, tris(2-methyl-3-propyl-hexyl)aluminium, tris(2-ethyl-



3-methyl-butyl)aluminium, tris(2-ethyl-3-methyl-pentyl)aluminium, tris(2,3-diethyl-pentyl)aluminium, tris(2-propyl-3-methyl-butyl)aluminium, tris(2-isopropyl-3-methyl-butyl)aluminium, tris(2-isobutyl-3-methyl-pentyl)aluminium, tris(2,3,3-trimethyl-pentyl)aluminium, tris(2,3,3-trimethyl-hexyl)aluminium, tris(2-ethyl-3,3-dimethyl-butyl)aluminium, tris(2-ethyl-3,3-dimethyl-pentyl)aluminium, tris(2-isopropyl-3,3-dimethyl-butyl)aluminium, tris(2-trimethylsilyl-propyl)aluminium, tris(2-methyl-3-phenyl-butyl)aluminium, tris(2-ethyl-3-phenyl-butyl)aluminium, tris(2,3-dimethyl-3-phenyl-butyl)aluminium, tris(2-phenyl-propyl)aluminium, tris[2-(4-fluoro-phenyl)-propyl]aluminium, tris[2-(4-chloro-phenyl)-propyl]aluminium, tris[2-(3-isopropyl-phenyl)-propyl]aluminium, tris(2-phenyl-butyl)aluminium, tris(3-methyl-2-phenyl-butyl)aluminium, tris(2-phenyl-pentyl)aluminium, tris[2-(pentafluorophenyl)-propyl]aluminium, tris[2,2-diphenyl-ethyl]aluminium and tris[2-phenyl-2-methyl-propyl]aluminium, as well as the corresponding compounds wherein one of the hydrocarbyl groups is replaced with a hydrogen atom, and those wherein one or two of the hydrocarbyl groups are replaced with an isobutyl group.

Amongst the above aluminium compounds, trimethylaluminium (TMA), triisobutylaluminium (TIBAL), tris(2,4,4-trimethyl-pentyl)aluminium (TIOA), tris(2,3-dimethylbutyl)aluminium (TDMBA) and tris(2,3,3-trimethylbutyl)aluminium (TTMBA) are preferred.

Non-limiting examples of compounds able to form an alkylmetallocene cation are compounds of formula  $D^+E^-$ , wherein  $D^+$  is a Brønsted acid, able to donate a proton and to react irreversibly with a substituent X of the metallocene of formula (I) and  $E^-$  is a compatible anion, which is able to stabilize the active catalytic species originating from the reaction of the two compounds, and which is sufficiently labile to be able to be removed by an olefinic monomer. Preferably, the anion  $E^-$  comprises of one or more boron atoms. More preferably, the anion  $E^-$  is an anion of the formula  $BAr_4^{(-)}$ , wherein the substituents Ar which can be identical or different are aryl radicals such as phenyl, pentafluorophenyl or bis(trifluoromethyl)phenyl. Tetrakis-pentafluorophenyl borate is particularly preferred examples of these compounds are described in WO 91/02012. Moreover, compounds of the formula  $BAr_3$  can conveniently be used. Compounds of this type are described, for example, in the published International patent application WO 92/00333. Other examples of compounds able to form an alkylmetallocene cation are compounds of formula  $BAr_3P$  wherein P is a substituted or unsubstituted pyrrol radicals. These compounds are described in WO01/62764. Other examples of cocatalyst can be found in EP 775707 and DE 19917985. Compounds

containing boron atoms can be conveniently supported according to the description of DE-A-19962814 and DE-A-19962910. All these compounds containing boron atoms can be used in a molar ratio between boron and the metal of the metallocene comprised between about 1:1 and about 10:1; preferably 1:1 and 2:1; more preferably about 1:1.

Non limiting examples of compounds of formula  $D^+E^-$  are:

Triethylammoniumtetra(phenyl)borate,  
 Tributylammoniumtetra(phenyl)borate,  
 Trimethylammoniumtetra(tolyl)borate,  
 Tributylammoniumtetra(tolyl)borate,  
 Tributylammoniumtetra(pentafluorophenyl)borate,  
 Tributylammoniumtetra(pentafluorophenyl)aluminate,  
 Tripropylammoniumtetra(dimethylphenyl)borate,  
 Tributylammoniumtetra(trifluoromethylphenyl)borate,  
 Tributylammoniumtetra(4-fluorophenyl)borate,  
 N,N-Dimethylaniliniumtetra(phenyl)borate,  
 N,N-Diethylaniliniumtetra(phenyl)borate,  
 N,N-Dimethylaniliniumtetrakis(pentafluorophenyl)borate,  
 N,N-Dimethylaniliniumtetrakis(pentafluorophenyl)aluminate,  
 Di(propyl)ammoniumtetrakis(pentafluorophenyl)borate,  
 Di(cyclohexyl)ammoniumtetrakis(pentafluorophenyl)borate,  
 Triphenylphosphoniumtetrakis(phenyl)borate,  
 Triethylphosphoniumtetrakis(phenyl)borate,  
 Diphenylphosphoniumtetrakis(phenyl)borate,  
 Tri(methylphenyl)phosphoniumtetrakis(phenyl)borate,  
 Tri(dimethylphenyl)phosphoniumtetrakis(phenyl)borate,  
 Triphenylcarbeniumtetrakis(pentafluorophenyl)borate,  
 Triphenylcarbeniumtetrakis(pentafluorophenyl)aluminate,  
 Triphenylcarbeniumtetrakis(phenyl)aluminate,  
 Ferroceniumtetrakis(pentafluorophenyl)borate,  
 Ferroceniumtetrakis(pentafluorophenyl)aluminate.  
 Triphenylcarbeniumtetrakis(pentafluorophenyl)borate,  
 N,N-Dimethylaniliniumtetrakis(pentafluorophenyl)borate,

Organic aluminum compounds used as compound c) are those of formula  $H_jAlU_{3-j}$  or

$H_jAl_2U_{6-j}$  described above.

The catalysts system used in the process of the present invention can also be supported on an inert carrier. This is achieved by depositing the metallocene compound a) or the product of the reaction thereof with the component b), or the component b) and then the metallocene compound a) on an inert support such as, for example, silica, alumina, Al-Si, Al-Mg mixed oxides, magnesium halides, organic polymer, preferably polyolefins such as styrene/divinylbenzene copolymers, polyethylene or polypropylene. The supportation process is carried out in an inert solvent such as hydrocarbon for example toluene, hexane, pentane or propane and at a temperature ranging from 0°C to 100°C, preferably the process is carried out at a temperature ranging from 25°C to 90°C.

A suitable class of supports which can be used is that constituted by porous organic supports functionalized with groups having active hydrogen atoms. Particularly suitable are those in which the organic support is a partially crosslinked styrene polymer. Supports of this type are described in European application EP 633 272.

Another class of inert supports particularly suitable for use according to the invention is that of polyolefin porous prepolymers, particularly polyethylene.

A further suitable class of inert supports for use according to the invention is that of porous magnesium halides such as those described in International application WO 95/32995.

The solid compound thus obtained, in combination with the further addition of the alkylaluminium compound either as such or prereacted with water if necessary, can be usefully employed in the gas-phase polymerization.

The process for the polymerization of olefins according to the invention can be carried out in the liquid phase in the presence or absence of an inert hydrocarbon solvent, or in the gas phase; preferably, the process is carried out in the gas phase. The hydrocarbon solvent can either be aromatic such as toluene, or aliphatic such as propane, hexane, heptane, isobutane or cyclohexane.

The polymerization temperature is generally comprised between -100°C and +100°C and, particularly between 10°C and +90°C. The polymerization pressure is generally comprised between 0.5 and 100 bar.

The lower the polymerization temperature, the higher are the resulting molecular weights of the polymers obtained.

The polymerization yields depend on the purity of the metallocene compound of the catalyst. The metallocene compounds obtained by the process of the invention can therefore be used as

such or can be subjected to purification treatments.

The components of the catalyst can be brought into contact with each other before the polymerization. The pre-contact concentrations are generally between 0.1 and  $10^{-8}$  mol/l for the metallocene component a), while they are generally between 2 and  $10^{-8}$  mol/l for the component b). The pre-contact is generally effected in the presence of a hydrocarbon solvent and, if appropriate, of small quantities of monomer. In the pre-contact it is also possible to use a non-polymerizable olefin such as isobutene, 2-butene and the like.

The molecular weight distribution can be varied by using mixtures of different metallocene compounds or by carrying out the polymerization in several stages which differ as to the polymerization temperature and/or the concentrations of the molecular weight regulators and/or the monomers concentration. Moreover by carrying out the polymerization process by using a combination of two different metallocene compounds of formula (I) a polymer endowed with a broad melting point is produced.

In the copolymers obtainable by the process of the invention, the content of ethylene derived units is between 1% by mol and 99.9% by mol; preferably it is between 40% by mol and 98% by mol; and more preferably it is between 50% by mol and 98% by mol.

The content of alpha-olefins derived units is between 0.1% by mol and 99% by mol; preferably it is between 2% by mol and 60% by mol; and more preferably it is between 5% by mol and 50% by mol.

Non-limiting examples of alpha-olefins of formula  $\text{CH}_2=\text{CHZ}$  which can be used as alpha-olefins in the process of the invention are 1-butene, 1-pentene, 4-methyl-1-pentene, 1-hexene, 1-octene, 4,6-dimethyl-1-heptene, 1-decene, 1-dodecene, 1-tetradecene, 1-hexadecene, 1-octadecene and 1-eicosene. Preferred comonomers are 1-pentene, 1-hexene and 1-octene.

The content of polyene derived units, if any, is preferably comprised between 0% and 5% by mol, and more preferably between 0 mol% and 3 mol%.

The polyenes that can be used as comonomers in the copolymers according to the present invention are included in the following classes:

- non-conjugated diolefins able to cyclopolymerize such as, for example, 1,5-hexadiene, 1-6-heptadiene, 2-methyl-1,5-hexadiene;
- dienes capable of giving unsaturated monomeric units, in particular conjugated dienes such as, for example, butadiene and isoprene, and linear non-conjugated dienes, such as, for example, trans 1,4-hexadiene, cis 1,4-hexadiene, 6-methyl-1,5-heptadiene, 3,7-dimethyl-1,6-octadiene, 11-methyl-1,10-dodecadiene, and cyclic non-conjugated dienes

such as 5-ethylidene-2-norbornene.

With the process of the present invention it is possible to obtain, in high yields, copolymers having a high molecular weight (I.V.) that makes the process object of the present invention fit for an industrial use. Moreover, since the use of the metallocene compounds of formula (I) gives rise to a high comonomer incorporation, this allows to use smaller concentration of the comonomer in the reactor and provides a more tunable process.

The intrinsic viscosity values of the copolymers obtained with the process of the present invention are generally higher than 0.5 dL/g, and preferably they range from 1.5 to 10 dL/g.

The following examples are given for illustrative purposes and do not intend to limit the invention.

## EXAMPLES

### *General procedures*

All operations were performed under nitrogen by using conventional Schlenk-line techniques. Heptane and toluene were purified by degassing with N<sub>2</sub> and passing over activated (8 hours, N<sub>2</sub> purge, 300 °C) Al<sub>2</sub>O<sub>3</sub>, and stored under nitrogen. 1-hexene (Aldrich) was dried over alumina and distilled over LiAlH<sub>4</sub>. Polymerization grade ethylene was obtained from the Basell Ferrara plant. MAO (methylalumoxane, Witco) was purchased as a 10 wt.-% solution in toluene, dried under vacuum to remove most of the free trimethylaluminum and used as 1 M toluene solution. TIBA (Al(*i*-Bu)<sub>3</sub>, Witco) was used as 1 M toluene solution.

<sup>1</sup>H-NMR spectra of copolymers were recorded at 120°C on a Bruker DPX-400 spectrometer operating at 100.61 MHz, in the Fourier transform mode. The samples were prepared by dissolution of 10 mg of copolymer in 0.5 mL of 1,1,2,2-tetrachloroethane-*d*<sub>2</sub> at 120 °C. When the end-group analysis had to be performed, the samples were prepared under inert atmosphere. The peak of C<sub>2</sub>HDCl<sub>2</sub> (5.95 ppm) was used as internal standard. Each spectrum was acquired with a 45° pulse and 20 seconds of delay between pulses (or 5 seconds when the end-group analysis had to be performed). About 16 transients (or 1K when the end-group analysis had to be performed) were stored in 32K data points using a spectral window of 16 ppm.

The 1-hexene content in the copolymers was calculated from the methylene and methyne peak integral (I<sub>A</sub>) and the methyl peak integral (I<sub>B</sub>), by applying the following relationships:

$$[C_6] = I_B/3$$

$$[C_2] = (I_A - 3I_B)/4$$

$$\Sigma = [C_6] + [C_2] = (I_B/3) + (I_A - 3I_B)/4$$

$$C_{6 \text{ copol}} (\% \text{ mol}) = 100 \times [C_6] / \Sigma = 100 \times I_B / 3\Sigma$$

The molecular weight distribution was determined on a WATERS 150 C using the following chromatographic conditions:

Columns: 3x SODEX AT 806 MS; 1x SODEX UT 807; 1x SODEX AT-G;  
 Solvent: 1,2,4 trichlorobenzene (+0.025% 2,6-di-*tert*-butyl-4-methyl-phenol)  
 Flow rate: 0.6-1 mL/min  
 Temperature: 135°C  
 Detector: Infrared at  $\lambda \cong 3.5 \mu\text{m}$

Calibration: Universal Calibration with PS-Standard

The intrinsic viscosity (I.V.) was measured in decaline (DHN) at 135°C.

The melting point ( $T_m$ ) and glass transition temperatures ( $T_g$ ) were determined on a DSC30 Mettler instrument equipped with a cooling device, by heating the sample from 25°C to 200°C at 20°C/min, holding for 10 min at 200°C, cooling from 200°C to -140°C, the peak temperature was taken as crystallization temperature ( $T_c$ ). Holding for 2 min at -140°C, heating from -140°C to 200°C at 20°C/min. The reported values are those determined from the second heating scan. The area of the second scan was taken as global melting enthalpy ( $\Delta H_f$ ).

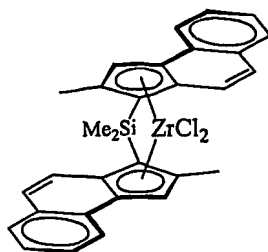
In cases in which crystallization phenomena overlap with the glass transition, for a best determination of the  $T_g$  value, the samples were heated at 200°C with a scanning speed corresponding to 20°C/minute, quickly cooled to a temperature lower than the  $T_m$  (usually 20, 0 or -20°C) at 200°C/minute, and kept at this temperature for 720 minutes. The samples were then further quickly cooled to -140°C with a scanning speed corresponding to 200°C/minute and finally re-heated to 200°C with a scanning speed corresponding to 20°C/minute. All the process was carried out under nitrogen flow of 20 mL/minute.

#### ***Determination of liquid phase composition***

The liquid phase composition was calculated from the Redlich-Kwong-Soave. This set of thermodynamic equations was selected among those available in Aspen Plus<sup>TM</sup> (commercialized by Aspen Technology Inc., Release 9) on the basis of a comparison with the experimental results. The concentrations of the comonomers were hence calculated.

#### **METALLOCENE COMPOUNDS**

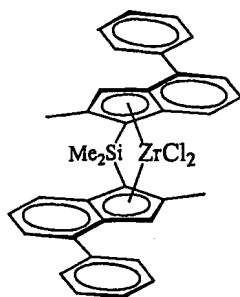
Dimethylsilylbis(2-methyl-4, 5-benzo-1-indenyl)zirconium dichloride [C1]



[C1]

was prepared as described in USP 5,830,821.

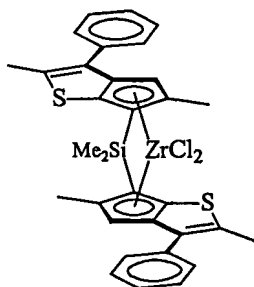
Dimethylsilylbis(2-methyl-4-phenyl-1-indenyl)zirconium dichloride [C2]



[C2]

was prepared as described in USP 5,786,432.

Dimethylsilylbis (2,5-dimethyl-3-phenyl-cyclopento[2,3-b]thiophen-6-yl) zirconium dichloride [A1]



[A1]

was prepared as described in WO 01/44318

### Polymerization Examples 1-9

#### General procedure

Ethylene/1-hexene copolymerizations were carried out in a 260-mL Büchi glass autoclave equipped with magnetic stirrer, thermocouple and feeding line for the monomer, purified with nitrogen and kept in a thermostatic bath. Heptane and 1-hexene (150 mL of total volume, amount of 1-hexene is reported in table 1) and triisobutylaluminum (TIBA) (0.5 mmol) were introduced and warmed to 70°C, then the autoclave was purged with ethylene. The catalytic system was separately prepared in 5 mL of toluene by mixing the amounts of metallocene reported in table 1 and methylalumoxane (MAO) (MAO/Zr ratio 500

mol/mol). After about 30 sec of stirring at room temperature, the solution was introduced into the autoclave under ethylene flow. The reactor was closed and pressurized at 4 bar-g; the temperature was raised to 70°C and the pressure was kept constant by feeding in ethylene. The polymerization was stopped after the time indicated in table 1 by degassing the reactor and by adding 2 mL of methanol. The polymer was precipitated with 200 mL of acetone, filtered, washed with acetone and dried overnight at 60°C under reduced pressure. Polymerization and polymer data are reported in table 1.

#### **Polymerization Example 10**

Supported catalyst containing Al was prepared according to example 50 of WO01/44318, The analysis of the obtained supported catalyst is: 5.75% wt. Al and 470 ppm Zr, with an Al/Zr molar ratio of 412.

A 4L autoclave, equipped with a blade turbine magnetic stirrer, pressure indicator, temperature indicator, system for loading the catalyst, feed line for monomer equipped with a thermal-mass flowmeter for the measure of the ethylene uptake and a thermosetting jacket, was used. At room temperature 2.5 mmol of TIBA (100g/L hexane solution) as scavenger and 50g of 1-hexene were loaded, followed by 1.6 L of propane; then the reactor was pressurized with 5 bar of ethylene partial pressure. The polymerization was started by injecting the catalyst at 30°C. A prepolymerization step was carried out at 30°C for 30 minutes, then the temperature was raised up to 75°C and the ethylene partial pressure was increased to 10 bar. These conditions were maintained by continuously feeding ethylene for 2 hour. The obtained ethylene copolymer has a 1-hexene content of 10.9% by mol, a melting point of 112.7°C, I.V. of 2.76 dl/g, density of 0.9079 Kg/dm<sup>3</sup> and  $r_1 \times r_2 = 0.97$ .



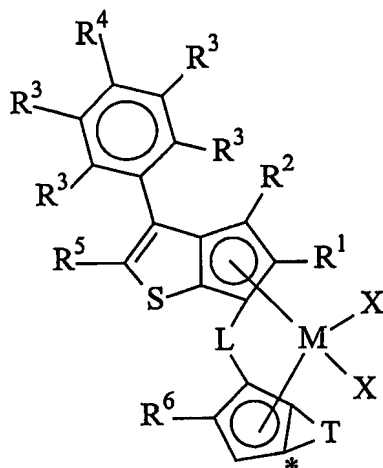
Table 1

Ex.	Metallocene		1-hexene		Yield (g)	Time (min)	Activity (K <sub>g</sub> pol/m mol <sub>Zr</sub> h)	C <sub>6</sub> content		Conversion (%) 100×(gC <sub>6</sub> copol/gC <sub>6</sub> feed)	I.V. (dL/g)	M <sub>w</sub> /M <sub>n</sub>	T <sub>g</sub> (°C)	T <sub>m</sub> (°C)	ΔH <sub>f</sub> (J/g)	T <sub>c</sub> (°C)
	type	μmol	(ml)	(g)				(%mol) exper.	(%wt) calc.							
1*	C2	0.2	2	1.32	0.5	5	30.6	10.3	25.7	9.9	2.96	2.48	-44.3	82.5	44.1	52.2
2*	C2	0.3	5	3.29	1.3	5	51.2	21.5	45.0	17.5	2.17	2.39	-51.3	n.d.	n.d.	2.0
3*	C2	0.3	10	6.59	1.1	7	30.3	32.6	59.2	9.5	1.72	2.51	-56.0	n.d.	n.d.	-50.0
4*	C1	0.25	2	1.32	1.2	3	95.2	7.7	20.0	18.1	2.59	2.56	-39.3	89.3	63.6	68.8
5*	C1	0.3	5	3.29	1.1	3	74.7	11.4	27.8	9.4	2.30	2.77	-49.1	66.6	37.7	46.2
6*	C1	0.3	10	6.59	0.7	3	43.3	18.9	41.1	4.1	1.91	2.24	-49.2	40.0	n.d.	4.9
7	A1	0.2	2	1.32	1.3	3	131.0	10.9	26.8	26.6	2.74	2.76	-47.4	68.5	41.6	47.9
8	A1	0.2	5	3.29	1.1	2	166.5	18.9	41.1	13.9	2.29	2.52	-52.5 <sup>#</sup>	35.4	43.4	5.8
9	A1	0.2	10	6.59	1.3	2	196.5	25.6	50.8	10.1	2.01	2.72	-55.7	n.d.	n.d.	-33.7

n.d. = not determinable. \* Comparative. <sup>#</sup> from melt crystallized sample

## CLAIMS

1. A process for producing a polymer of ethylene containing from 0.1 to 99 % by mol of one or more derived units of alpha-olefins of formula  $\text{CH}_2=\text{CHZ}$ , wherein Z is a  $\text{C}_2\text{-C}_{20}$  alkyl radical, and optionally from 0 to 5% by mol polyene, comprising contacting, under polymerization conditions, ethylene, one or more alpha-olefins and optionally said polyene, in the presence of a catalyst system obtainable by contacting:
  - a) a metallocene compound of formula (I):



(I)

wherein

M is zirconium, hafnium or titanium;

X, equal to or different from each other, is a hydrogen atom, a halogen atom, a R, OR, OR'O,  $\text{OSO}_2\text{CF}_3$ , OCOR, SR,  $\text{NR}_2$  or  $\text{PR}_2$  group, wherein R is a linear or branched, saturated or unsaturated  $\text{C}_1\text{-C}_{20}$ -alkyl,  $\text{C}_3\text{-C}_{20}$ -cycloalkyl,  $\text{C}_6\text{-C}_{20}$ -aryl,  $\text{C}_7\text{-C}_{20}$ -alkylaryl, or  $\text{C}_7\text{-C}_{20}$ -arylalkyl radical, optionally containing one or more heteroatoms belonging to groups 13-17 of the Periodic Table of the Elements; and the R' substituent is a divalent group selected from  $\text{C}_1\text{-C}_{40}$ -alkylidene,  $\text{C}_6\text{-C}_{40}$ -arylidene,  $\text{C}_7\text{-C}_{40}$ -alkylarylidene or  $\text{C}_7\text{-C}_{40}$ -arylalkylidene radicals; two X can join to form a  $\text{C}_4\text{-C}_{40}$  dienyl ligand;

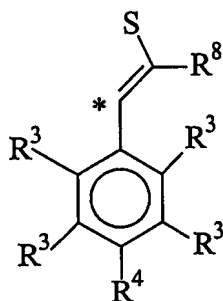
$\text{R}^1$  is a linear or branched, saturated or unsaturated  $\text{C}_1\text{-C}_{20}$ -alkyl,  $\text{C}_3\text{-C}_{20}$ -cycloalkyl,  $\text{C}_6\text{-C}_{20}$ -aryl,  $\text{C}_7\text{-C}_{20}$ -alkylaryl, or  $\text{C}_7\text{-C}_{20}$ -arylalkyl radical, optionally containing one or more heteroatoms belonging to groups 13-17 of the Periodic Table of the Elements;

$\text{R}^2$ ,  $\text{R}^3$ ,  $\text{R}^4$  and  $\text{R}^5$ , equal to or different from each other, are hydrogen atoms, halogen atoms or linear or branched, saturated or unsaturated  $\text{C}_1\text{-C}_{20}$ -alkyl,  $\text{C}_3\text{-C}_{20}$ -cycloalkyl,  $\text{C}_6\text{-C}_{20}$ -aryl,  $\text{C}_7\text{-C}_{20}$ -alkylaryl, or  $\text{C}_7\text{-C}_{20}$ -arylalkyl radicals, optionally containing one or more heteroatoms belonging to groups 13-17 of the Periodic Table of the Elements;

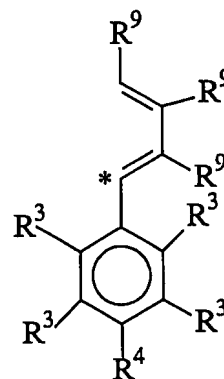
$R^6$  is a linear or branched, saturated or unsaturated  $C_1$ - $C_{20}$ -alkyl,  $C_3$ - $C_{20}$ -cycloalkyl,  $C_6$ - $C_{20}$ -aryl,  $C_7$ - $C_{20}$ -alkylaryl, or  $C_7$ - $C_{20}$ -arylalkyl radical, optionally containing one or more heteroatoms belonging to groups 13-17 of the Periodic Table of the Elements;

L is a divalent bridging group selected from  $C_1$ - $C_{20}$  alkylidene,  $C_3$ - $C_{20}$  cycloalkylidene,  $C_6$ - $C_{20}$  arylidene,  $C_7$ - $C_{20}$  alkylarylidene, or  $C_7$ - $C_{20}$  arylalkylidene radicals, optionally containing heteroatoms belonging to groups 13-17 of the Periodic Table of the Elements, or a silylidene radical containing up to 5 silicon atoms;

T is a divalent radical of formula (II) or (III):



(II)



(III)

wherein

the atom marked with the symbol \* is linked to the atom marked with the same symbol in the compound of formula (I);

$R^3$  and  $R^4$  have the meaning previously described;

$R^8$  is a hydrogen atom or a linear or branched, saturated or unsaturated  $C_1$ - $C_{20}$ -alkyl,  $C_3$ - $C_{20}$ -cycloalkyl,  $C_6$ - $C_{20}$ -aryl,  $C_7$ - $C_{20}$ -alkylaryl, or  $C_7$ - $C_{20}$ -arylalkyl radical, optionally containing one or more heteroatoms belonging to groups 13-17 of the Periodic Table of the Elements;

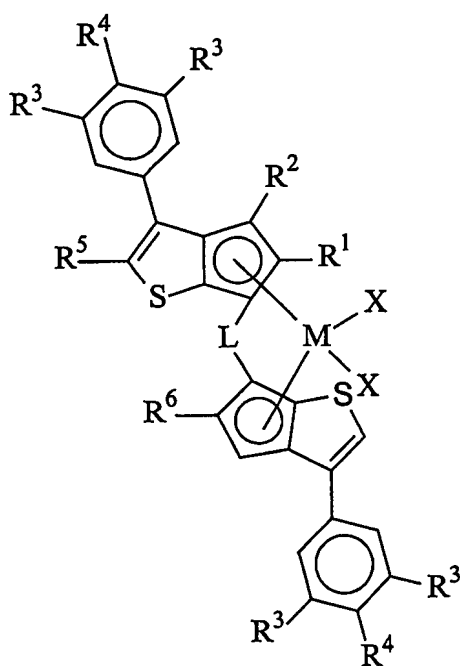
$R^9$ , equal to or different from each other, is a hydrogen atom or a linear or branched, saturated or unsaturated  $C_1$ - $C_{20}$ -alkyl,  $C_3$ - $C_{20}$ -cycloalkyl,  $C_6$ - $C_{20}$ -aryl,  $C_7$ - $C_{20}$ -alkylaryl, or  $C_7$ - $C_{20}$ -arylalkyl radical, optionally containing one or more heteroatoms belonging to groups 13-17 of the Periodic Table of the Elements; and

b) an alumoxane or a compound capable of forming an alkyl metallocene cation.

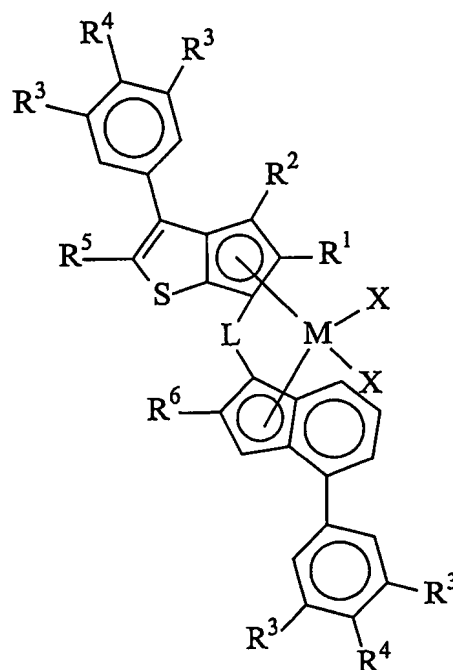
2. The process according to claim 1 wherein the catalyst system further comprises an organo aluminum compound.
3. The process according to claim 1 wherein in the compound of formula (I):

X is a halogen atom, a R, OR'O or OR group, wherein R and R' are defined as in claim 1; R<sup>1</sup> is a linear or branched, saturated or unsaturated C<sub>1</sub>-C<sub>20</sub>-alkyl radical; R<sup>2</sup> is a hydrogen atom; R<sup>3</sup> is a hydrogen atom or a linear or branched, saturated or unsaturated C<sub>1</sub>-C<sub>20</sub>-alkyl radical optionally containing one or more halogen atom; R<sup>4</sup> is a hydrogen atom or a linear or branched, saturated or unsaturated C<sub>1</sub>-C<sub>20</sub>-alkyl radical; R<sup>6</sup> is a linear or branched, saturated or unsaturated C<sub>1</sub>-C<sub>20</sub>-alkyl radical; L is Si(CH<sub>3</sub>)<sub>2</sub>, SiPh<sub>2</sub>, SiPhMe, SiMe(SiMe<sub>3</sub>), CH<sub>2</sub>, (CH<sub>2</sub>)<sub>2</sub>, (CH<sub>2</sub>)<sub>3</sub>, C(CH<sub>3</sub>)<sub>2</sub>, C(Ph)<sub>2</sub> or C(CH<sub>3</sub>)(Ph); R<sup>8</sup> is hydrogen or a linear or branched, saturated or unsaturated C<sub>1</sub>-C<sub>20</sub>-alkyl radical; and R<sup>9</sup> is hydrogen or a linear or branched, saturated or unsaturated C<sub>1</sub>-C<sub>20</sub>-alkyl radical.

4. The process according to claim 1 wherein the metallocene compound has formula (IV) or (V):



(IV)



(V)

wherein R<sup>1</sup>, R<sup>2</sup>, R<sup>5</sup>, R<sup>6</sup>, L, M and X have the meaning reported in claim 1 or 3;

R<sup>3</sup> is a hydrogen atom or a linear or branched, saturated or unsaturated C<sub>1</sub>-C<sub>10</sub>-alkyl radical, optionally containing one or more halogen atom; R<sup>4</sup> is a hydrogen atom or a linear or branched, saturated or unsaturated C<sub>1</sub>-C<sub>10</sub>-alkyl radical.

5. The process according to claim 4 wherein, in the compounds of formula (IV) and (V), R<sup>3</sup> is a hydrogen atom or a group -C(R<sup>7</sup>)<sub>3</sub>, wherein R<sup>7</sup>, equal to or different from each other, is a linear or branched, saturated or unsaturated C<sub>1</sub>-C<sub>8</sub>-alkyl radical; and R<sup>4</sup> is hydrogen or a group -C(R<sup>7</sup>)<sub>3</sub>.

6. The process according to any of claims 1 to 5 wherein, in the compounds of formulas (I), (IV) and (V),  $R^3$  and  $R^4$  are hydrogen atoms.
7. The process according to any of claims 1 to 5 wherein, in the compounds of formulas (I), (IV) and (V), when  $R^3$  is an hydrogen atom,  $R^4$  is or a linear or branched, saturated or unsaturated  $C_1$ - $C_{10}$ -alkyl radical, optionally containing one or more halogen atom; or when  $R^3$  is a linear or branched, saturated or unsaturated  $C_1$ - $C_{10}$ -alkyl radical optionally containing one or more halogen atom,  $R^4$  is an hydrogen atom.
8. The process according to any of claims 1 to 7 wherein the catalyst system is supported on an inert carrier.
9. The process according to claim 8 wherein the catalyst system is supported on a polyolefin.
10. The process according to any of claims 1 to 9 wherein the process is carried out in gas phase.
11. The process according to any of claims 1 to 11 wherein the alpha-olefin is 1-pentene, 1-hexene or 1-octene.

## A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 C08F210/02 C08F4/64

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C08F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, CHEM ABS Data

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 01 44318 A (BASELL TECHNOLOGY COMPANY B V ;EWEN JOHN A (US); ELDER MICHAEL J ( ) 21 June 2001 (2001-06-21) cited in the application page 30, line 10-17 page 31, line 25 -page 32, line 9 page 32, line 5 examples 1,2,4 claims	1-11
P,X	WO 02 100909 A (BASELL POLYOLEFINE GMBH ;RESONI LUIGI (IT)) 19 December 2002 (2002-12-19) page 9, line 26; examples 14-19 -/-	1-11

☒ Further documents are listed in the continuation of box C.☒ Patent family members are listed in annex.

## \* Special categories of cited documents:

- \*A\* document defining the general state of the art which is not considered to be of particular relevance
- \*E\* earlier document but published on or after the international filing date
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Date of the actual completion of the international search

21 November 2003

Date of mailing of the international search report

02/12/2003

Name and mailing address of the ISA

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Authorized officer

Baekelmans, D

## C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 02 100908 A (BASELL POLYOLEFINE GMBH ; RESCONI LUIGI (IT)) 19 December 2002 (2002-12-19) the whole document -----	1-11

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
WO 0144318	A	21-06-2001	US 6444833 B1	03-09-2002
			AU 3007901 A	25-06-2001
			BR 0010043 A	22-01-2002
			CA 2362093 A1	21-06-2001
			CN 1347424 T	01-05-2002
			WO 0144318 A1	21-06-2001
			EP 1153047 A1	14-11-2001
			JP 2003517010 T	20-05-2003
			PL 349318 A1	15-07-2002
			US 6635779 B1	21-10-2003
			ZA 200106367 A	04-11-2002
WO 02100909	A	19-12-2002	WO 02100909 A1	19-12-2002
WO 02100908	A	19-12-2002	WO 02100908 A1	19-12-2002